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<b>(54) Title:</b> GELLED NEAR TRICRITICAL POINT COMPOSITIONS  <b>(57) Abstract</b> <p>The present invention relates to an aqueous gelled cleaning composition which is useful for the removal of grease or tar without any mechanical action. In particular, the instant compositions are derived from three liquid phases which merge together at the tricritical point to form one continuum forming the gelled aqueous cleaning composition, wherein the three phases incorporate at least a polar solvent, a non-polar solvent or weakly polar solvent and a water soluble or water low molecular weight water dispersible amphiphile and the composition contains a noncross-linked polymer.</p>		

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## GELLED NEAR TRICRITICAL POINT COMPOSITIONS

Field of the Invention

5 The present invention relates to a gelled aqueous, cleaning composition which is optionally surfactant-free and is useful for the removal of grease or tar without any mechanical action. In particular, the instant compositions comprise three liquid phases which merge together in the vicinity of a tricritical point to form one continuum, wherein each of the three phases essentially contain a polar solvent, a non-polar solvent or a weakly polar solvent and a water soluble or water dispersible low  
10 molecular weight amphiphile.

Background of the Invention

Liquid aqueous synthetic organic detergent compositions have long been employed for human hair shampoos and as dishwashing detergents for hand washing of dishes (as distinguished from automatic dishwashing, machine washing of dishes).  
15 Liquid detergent compositions have also been employed as hard surface cleaners, as in pine oil liquids, for cleaning floors and walls. More recently, they have proven successful as laundry detergents too, apparently because they are convenient to use. are instantly insoluble in wash water, and may be employed in "pre-spotting" applications to facilitate removal of soils and stains from laundry upon subsequent  
20 washing. Liquid detergent compositions have comprised anionic, cationic and nonionic surface active agents, builders and adjuvants including, as adjuvants, lipophilic materials which can act as solvents for lipophilic soils and stains. The various liquid aqueous synthetic organic detergent compositions mentioned above serve to emulsify lipophilic materials including oily soils in aqueous media, such as  
25 wash water, by forming micellar dispersions and emulsions.

A cleaning action can be regarded as a more-or-less complex process resulting in the removal of soils from a given surface. The driving forces generally involved in this process are mechanical energy (friction, attrition, sonification, etc.), solvation by a liquid, thermal agitation, soil-solvent interfacial tension reduction, chemical

modifications (caustic, acidic, oxidative, reductive, hydrolysis, assisted or not by catalysts or enzymes), soil or soil residual suspension (e.g. in micellar solutions), and so on.

When the cleaning action takes place in water liquid vehicle, auxiliary cleaning agents, especially surfactants, are generally required to get rid of hydrophobic soils. Moreover, in most domestic cleaning tasks, the success of the cleaning mechanism is based on the reduction of the water/oil interfacial tension. The generally admitted theory is that the oily soil is easily dispersed or even solubilized in the composition because of the low interfacial tension existing between the composition and the oil.

Another explanation can be evoked. Due to the low interfacial tension, the liquid detergent composition easily diffuses through the soil or between the support and the soil, thereby weakening all bonding forces; the soil is then spontaneously removed from the substrate. This is the cause for the removal of oily soil without a real solubilization of the soil which eventually is emulsified. Both mechanisms are complementary in the cleaning process.

Although emulsification is a mechanism of soil removal, it has been recently discovered how to make microemulsions which are much more effective than ordinary emulsions in removing lipophilic materials from substrates. Such microemulsions are described in British Patent Specification No. 2,190,681 and U.S. Patent Applications Serial Nos. 06/866,029, 07/085,902, 07/120,250 and 07/267,872 most of which relates to acidic microemulsions useful for cleaning hard surface items such as bathtubs and sinks, which microemulsions are especially effective in removing soap scum and lime scale from them. In U.S. Patent Application Serial No. 07/267,872 the microemulsions may be essentially neutral and as such are also thought to be effective for microemulsifying lipophilic soils from substrates. In U.S. Patent Application Serial No. 07/313,664 there is described a light duty microemulsion liquid detergent composition which is useful for washing dishes and removing greasy deposits from them in both neat and diluted forms. Such compositions include

complexes of anionic and cationic detergents as surface active components of the microemulsions.

The various microemulsions referred to include a lipophile which may be a hydrocarbon, a surfactant which may be an anionic and/or a nonionic detergent(s), a co-surfactant which may be a poly-lower alkylene glycol lower alkyl ether, e.g. tripropylene glycol monomethyl ether, and water.

Although the manufacture and use of detergent compositions in microemulsion form significantly improves cleaning power and greasy soil removal, compared to the usual emulsions, the present invention improves them still further by the formation of aqueous near tricritical cleaning compositions which have improved cleaning as compared to microemulsions.

The instant aqueous cleaning compositions, which are optionally surfactant-free, provide increased grease and tar removal capabilities without or with a minimum mechanical action as compared to the water-based microemulsions as disclosed in U.S. Patents Nos. 5,075,026, 5,108,643; 4,919,839 and 5,082,584. These water-based microemulsions all contain a surfactant as compared to the preferred surfactant-free compositions of the instant invention.

In most domestic cleaning tasks, the success of the cleaning mechanism is based on reduction of the water/oil interfacial tension. In this frame, the thermodynamic of phases predict that ultra-low interfacial tensions can be reached in the direct vicinity of peculiar compositions called "critical points" and particularly near "tricritical points," the properties of which were extensively described by Griffiths (Robert B.) Wheeler (John C.), Critical points in multicomponent systems, Phys. Rev. A, NEW YORK 1970, 2, (3), (Sept.), pp.: 1047-1064; and Griffiths (Robert B.), Thermodynamic model for tricritical points in ternary and quaternary fluid mixtures. J. Chem. Phys., LANCASTER. 1974, 60, (1), pp.: 195-206; and Widom B. Tricritical points in three - and four - component fluid mixtures J. Phys. Chem., WASHINGTON. 1973, 77, (18), pp.: 2196-2200; and Widom (B.) Interfacial tensions of three fluid phases in equilibrium. J. Chem. Phys. Lancaster, 1975, 62 (4) pp: 1332-13360 and

Lang (J. C.) Widom (B.) Equilibrium of three liquid phases and approach to the tricritical point in benzene-ethanol-water-ammonium sulfate mixtures. Physica A, AMSTERDAM. 1975, 81A, pp.: 190-213; and Widom (B.) Three-phase equilibrium and the tricritical point. Kinan, MEXICO. 1981, 3, A, pp.: 143-157

5 It must be pointed out that, in such critical compositions, surfactants are not a must. Moreover, it is not absolutely essential to be right at a tricritical point to obtain surface tensions much lower than those currently achieved with today's cleaning systems.

It is worthwhile to note that the tricritical points theory has already been under  
10 high scrutiny in view of enhancing oil recovery. These works are extensively described by Fleming (P. D.) Vinatieri (J. E.). Phase behavior of multicomponent fluids. J. Phys. Chem., WASHINGTON. 1977, 66, (7), pp.: 3147-3154 and Vinatieri (James E.) Fleming (Paul D.). Use of pseudocomponents in the representation of phase behavior of surfactant systems. Soc. Pet. Eng. J., DALLAS, 1979, 19, pp.:  
15 289-300; and Fleming (Paul D.) Vinatieri (James E.). Quantitative interpretation of phase volume behavior of multicomponent systems near critical points. AIChE J., NEW YORK 1979, 25, (3), pp.: 493-502; and Fleming (Paul D.) Vinatieri (James E.). Role of critical phenomena in oil recovery systems employing surfactants. J. Colloid Interface Sci., NEW YORK. 1981, 81, (2), pp.: 319-331; and Vinatieri (James) Fleming (Paul D.).  
20 Multivariate optimization of surfactant systems for tertiary oil recovery. Soc. Pet. Eng. J., DALLAS. 1981, (2), pp.: 77-88; and Smith (Duane H.). Interfacial tensions near the tricritical points of classical liquids: experimental evidence for the validity of the prediction of critical scaling theory. J. Chem. Phys., LANCASTER 1986, 85, PP.: 1545-1558. and Smith (Duane H.). Tricritical points as an aid to the design of  
25 surfactants for low-tension enhanced oil recovery. AOSTRA J. Res., EDMONTON(Alberta) 1984, (4), pp: 245-265.

In 1926, Kohnstamm rose the theoretical possibility of a critical point "of the second order" in a ternary liquid mixture, a point at which three co-existing fluid phases merge and become identical, Kohnstamm (Ph.). Handbuch der physik, 1926,

Vol. 10, Kap. 4, Thermodynamik der Gemische, pp. 270-271, H. Geiger and K. Scheel (SPRINGER, BERLIN). Kohnstamm also stressed the extreme difficulty to find such a point.

The aqueous cleaning near tricritical point compositions of the instant invention are applicable for use in concentrated household care products and personal care products. The near tricritical point compositions of the instant invention comprise harmless ingredients. The instant near tricritical point compositions permit the preparation of cleaning or conditioning liquid products which are optionally surfactant-free.

In accordance with the present invention, a gelled near tricritical point cleaning composition, suitable at room temperature or colder or at a higher temperature for pre-treating and cleaning materials soiled with a lipophilic soil, comprises a polar solvent such as water, a water soluble or dispersible low molecular weight amphiphile, and a non-polar solvent, or weakly polar solvent wherein the three phases have merged into one continuum at the tricritical point as well as a low molecular weight non crosslinked polymer. The invention also relates to processes for treating items and materials soiled with soils such as lipophilic soil, with compositions of this invention, to loosen and to remove without mechanical action such soil by applying to the locus of such soil on such material a soil loosening or removing amount of the tricritical point compositions of the instant invention.

The instant aqueous gelled cleaning composition exists at or in the vicinity of the tricritical point which is the terminus of three lines of critical points. The tricritical point is a thermodynamical point at which all three co-existing phases become identical simultaneously. At the tricritical point, the interfacial tension between the merging phases of the polar solvent (water) and the low molecular weight amphiphile is substantially zero, and the interfacial tension between the merging phases of the low molecular weight amphiphile and non-polar solvent (oil) or a weakly polar solvent is substantially zero, and the interfacial tension between the polar solvent and the non-polar or weakly polar solvent is substantially zero. Accordingly, the cleaning

mechanism of the cleaning compositions of the instant invention is based on the reduction of the polar solvent/non-polar solvent interfacial tension as it approaches the value of zero.

The gelled compositions of the instant invention have a phase inversion temperature (PIT) of 0 to 80°C, more preferably 15 to 40°C. The phase inversion temperature is the temperature at which there is an equal affinity of the low molecular weight amphiphile for water and for oil. It is the temperature at which the partition of the low molecular weight amphiphile between the water rich phase and the non-polar solvent phase or weakly polar solvent phase equals unity. That is, the weight fraction of the low molecular weight amphiphile in the water rich phase is equal to the weight fraction of the low molecular weight amphiphile in the non-polar solvent phase.

The gelled tricritical point compositions have

$$\text{a ratio } (\alpha) = \frac{\text{wt \% of oil}}{\text{wt \% of water} + \text{wt \% of oil} + \text{wt. \% of additives}}$$

$$\text{and a ratio } (\gamma) = \frac{\text{wt \% of low molecular weight amphiphile}}{100 \text{ wt \% of composition}}$$

$$\text{and a ratio } (\epsilon) = \frac{\text{wt \% of additive}}{\text{wt \% of water} + \text{wt. \% of additive}}$$

wherein the weight fraction of the water is equal to  $(1-\gamma)(1-\alpha)(1-\epsilon)$  and  $\alpha$  is 0.01 to 0.50 more preferably 0.05 to 0.30,  $\gamma$  is 0.01 to 0.40, more preferably 0.03 to 0.25, and  $\epsilon$  is 0 to 0.20, more preferably 0.01 to 0.05, wherein the additive is a water soluble additive, a polar co-solvent or an electrolyte.

The additives are water soluble molecules (electrolytes or organics) that are able to modify the structure of water so as to strengthen or disrupt the solvent structure. Addition of such chemicals will therefore modify the solubility of uncharged organic ingredients in water and, among others, of amphiphilic molecules. The above chemicals are divided into two classes: Salting-out (or kosmotropic) agents reinforce the structure of water and make it less available to hydrate organic molecules. (Salting-out and -in agents are also referred to as lyotropes and hydrotropes,



respectively.) Salting-in (or chaotropic) agents, on the other hand, disorder the structure of water, thereby creating an effect comparable to "holes." As a consequence they increase the solubility of polar organic molecules in water.

5 In practice, lyotropic agents make water more incompatible with both oil and amphiphile. The result is a decrease of the PIT and an increase of the supercritical character. The amount of low molecular weight amphiphile needed to "congregate" water and oil generally increases in the presence of salting-out agents. Hydrotropic agents have the opposite effects.

#### Summary of the Invention

10 The instant invention relates to an aqueous gelled near tricritical point composition having a Brookfield viscosity at 25°C, #4 spindle, 20 rpms 150 to 10,000 cps, more preferably 500 to 6,000 cps, and a surface tension of 10 to 35 mN/m, which comprises by weight 55 to 95 wt % of a polar solvent; 1 to 15 wt % of a non-polar solvent or a weakly polar solvent, and 1 to 23 wt % of water soluble or water  
15 dispersible low molecular weight amphiphile and 0.2 to 3 wt. % of a low molecular weight noncrosslinked polymer selected from the group consisting of a polyacrylic acid type polymer and a polyacrylamide type polymer, wherein the polymer has a molecular weight of 20000 to 800000.

Accordingly, it is an object of the instant invention to provide an aqueous  
20 tricritical point cleaning composition which is useful in a cleaning operation without or with a minimum of mechanical action for the removal of grease and tar and especially for the penetration of the near tricritical composition into a porous surface thereby destroying the adhesion of soil to the substrate.

#### Detailed Description of the Invention

25 The present invention relates to an aqueous near tricritical point composition having a Brookfield viscosity at 25°C, #4 spindle, 20 rpms 150 to 10,000 cps, more preferably 500 to 6,000 cps, and a surface tension of 10 to 35 mN/m, which comprises by weight:

a) 2 to 15% of a non-polar solvent or a weakly polar solvent or mixtures thereof, more preferably 2 to 12% and most preferably 2 to 10%;

b) 1 to 23%, more preferably 2 to 20% and most preferably 3 to 18%, of a water soluble or water low molecular weight dispersible amphiphile;

5 c) 55 to 95%, more preferably 70 to 94% and most preferably 74 to 94%, of a polar solvent, wherein the composition is optionally surfactant-free;

d) 0.2 to 3 wt. % of a low molecular weight noncrosslinked polymer selected from the group consisting of a polyacrylic acid type polymer and a polyacrylamide type polymer, wherein the polymer preferably has a molecular  
10 weight of 20000 to 800000; and

(e) 0 to 20%, more preferably 0.5 to 15% and most preferably 1.0 to 10% of a water soluble additive, wherein the composition can optionally contain at least one solid particle and/or immiscible solvent which is not the non-polar or weakly polar solvent in the gelled composition.

15 The gelled tricritical point compositions of the instant invention have three coexisting liquid phases that are capable of being converted into one single phase by weak mechanical action according to a reversible equilibrium or to make the three coexisting liquid phases merge together into one continuum to form the tricritical point composition.

20 In the following section, all mentions of wt. % concentrations ( $X_1$ ,  $X_2$ ,  $X_3$ ,  $X$ ,  $Y_1$ ,  $Y_2$ ,  $Y_3$ ,  $Z_1$ ,  $Z_2$ ,  $Z_3$ ) are expressed with reference to the whole gelled composition and not reference to the considered singular phase. The wt. % concentration of the polar solvent in the first phase is represented by  $X_1$  and the wt. % concentration of the polar solvent in the second phase is represented by  $X_2$  and the wt. % concentration of the  
25 polar solvent in the third phase is represented by  $X_3$ , wherein the total wt. % concentration ( $X$ ) of the polar solvent in the composition is equal to  $X_1 + X_2 + X_3$ , wherein  $X_1$ ,  $X_2$  and  $X_3$  are equal to each other. The concentration of the polar solvent can tolerate variations of  $\pm 5$  absolute wt. % (i.e. with reference to the whole composition = 100%), more preferably by  $\pm 2$  absolute wt. % and most preferably  $\pm 1$

absolute wt. % in each of the three phases. For example, if the total concentration of the polar solvent in the composition is 81 wt. %, the concentration of the polar solvent in each of the three phases is 22 wt. % to 32 wt. %, more preferably 25 wt. % to 29 wt. % and most preferably 26 wt. % to 28 wt. %, wherein  $X_1 > X_2$  or  $X_3$ .

- 5           The wt. % concentration of the water soluble or water dispersible low molecular weight amphiphile in the first phase is represented by  $Y_1$  and the wt. % concentration of the amphiphile in the second phase is represented by  $Y_2$  and the wt. % concentration of the amphiphile in the third phase is represented by  $Y_3$ , wherein the total wt. % concentration ( $Y$ ) of the amphiphile in the composition is equal to
- 10  $Y_1 + Y_2 + Y_3$ , wherein  $Y_1$ ,  $Y_2$  and  $Y_3$  are equal to each other. The concentration of the low molecular weight amphiphile can tolerate variations of  $\pm 2$  absolute wt. % and more preferably  $\pm 1$  absolute wt. % in each of the three phases. For example, if the total concentration of the low molecular weight amphiphile in the composition is 9 wt. %, the concentration of the polar solvent in each of the three phases is 1 wt. % to 5 wt. %
- 15 %, more preferably 2 wt. % to 4 wt. %, wherein  $Y_2 > Y_1$  or  $Y_3$ .

- The wt. % concentration of the non-polar solvent (also weakly polar solvent) in the first phase is represented by  $Z_1$  and the wt. % concentration of the non-polar solvent in the second phase is represented by  $Z_2$  and the wt. % concentration of the non-polar in the third phase is represented by  $Z_3$ , wherein the total wt. %
- 20 concentration ( $Z$ ) of the non-polar solvent in the composition is equal to  $Z_1 + Z_2 + Z_3$ , wherein  $Z_1$ ,  $Z_2$  and  $Z_3$  are equal to each other. The concentration of the nonpolar solvent can tolerate variations of  $\pm 5$  absolute wt. %, more preferably  $\pm 2$  absolute wt. % and most preferably  $\pm 1$  absolute wt. % in each of the three phases. For example, if the total concentration of the low molecular weight amphiphile in the composition is 9 wt. %
- 25 %, the concentration of the polar solvent in each of the three phases is 1 wt. % to 5 wt. %, more preferably 2 wt. % to 4 wt. %, wherein  $Z_3 > Z_1$  or  $Z_2$ .

The tricritical point gelled compositions unlike true microemulsions which are optically clear exhibit a critical opalescence in that the tricritical point composition appears opalescent.

5 When the tricritical point composition is at the tricritical point the three phases merge into one single phase, wherein  $X_1=X_2=X_3$  and  $Y_1=Y_2=Y_3$  and  $Z_1=Z_2=Z_3$  in the single phase.

The aqueous gelled near tricritical point compositions of the instant invention can be used as a basic formulation for the production of both commercial and industrial applications by the incorporation of selective ingredients in the tricritical  
10 point composition. Typical gelled compositions which can be formed for a variety of applications are oral compositions, cosmetics, hand creams, facial creams, eye shadows, lipsticks, metal polish agents, fabric cleaners, shampoos, floor cleaners, cleaning pastes, tile cleaners, bath tub cleaners, bleach compositions, ointments, oven cleaners, stain removers, fabric softeners, bleach pre-spotters, dishwashing  
15 prespotters, automatic dishwashing compositions, laundry pre-spotters, pharmaceutical compositions, coal slurries, oil drilling muds, and cleaning pre-spotters and graffiti or paint removers, mildew cleaner for grouts, flux removers for printed circuit boards, engine cleaners and degreasers, deinking compositions for printing machines and shoreline cleaners for shorelines contaminated by spilled  
20 crude oil as well as any composition containing an active ingredient which active ingredient has to be delivered into a cavity or a porous surface for either a cleaning mechanism or for the delivery of a medical use for medical treatment such as in treatment of oral diseases.

The present invention relates to a gelled liquid cleaning composition which is  
25 optionally surfactant-free having a surface tension of 10 to 35 mN/m at 25°C deriving from three co-existing liquid phases which are almost chemically identical to each other and the three co-existing liquid phases have merged together into one continuum to form the composition, wherein the first phase has the most polar solvent, the second phase has the most water soluble or water dispersible amphiphile and the

third phase has the most non-polar solvent or weakly polar solvent and the interfacial tension between said first phase and said second phase is 0 to  $1 \times 10^{-3}$  mN/m and the interfacial tension between the second phase and the third phase is 0 to  $1 \times 10^{-3}$  mN/m, and the interfacial tension between the first phase and the third phase is 0 to  $1 \times 10^{-3}$  mN/m.

In a preferred gelled composition, the polar solvent is water at a concentration of 55 to 95 wt %, the low molecular weight amphiphile is an organic compound having a water insoluble hydrophobic portion which has a partial Hansen polar parameter and hydrogen bonding parameter, both of which are less than  $5 \text{ (MPa)}^{1/2}$ , and a water soluble hydrophilic portion which has a partial Hansen hydrogen bonding solubility parameter greater than  $10 \text{ (MPa)}^{1/2}$ ; the amphiphile is present at a concentration of 1 to 23 wt %; and non-polar solvent or weakly polar solvent has a Hansen dispersion solubility parameter greater than  $10 \text{ (MPa)}^{1/2}$  and a Hansen hydrogen bonding solubility parameter of less than  $15 \text{ (MPa)}^{1/2}$ , being present at a concentration of 2 to 15 wt %.

The main characteristic of the polar solvent is that it has the ability to form hydrogen bonding with the low molecular weight amphiphile and the polar solvent has a dielectric constant of higher than 35. Besides water, other polar solvents suitable for use in the instant composition are formamide, glycerol, glycol and hydrogen peroxide and mixtures thereof. The aforementioned polar solvents can be mixed with water to form a mixed polar solvent system. The concentration of the polar solvent such as water in the near tricritical point composition is 55 to 95 wt %, more preferably 70 to 94 wt %.

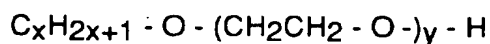
The organic non-polar or weakly polar solvent component of the present aqueous gelled near tricritical point compositions includes solvents for the soils, is lipophilic. The non-polar solvent or weakly polar solvent has a Hansen dispersion solubility parameter at  $25^{\circ}\text{C}$  of at least  $10 \text{ (MPa)}^{1/2}$ , more preferably at least  $14.8 \text{ (MPa)}^{1/2}$ , a Hansen polar solubility parameter of less than  $10 \text{ (MPa)}^{1/2}$  and a Hansen hydrogen bonding solubility parameter of less than  $15 \text{ (MPa)}^{1/2}$ . In the selection of

the non-polar solvent or weakly polar solvent, important parameters to be considered are the length and configuration of the hydrophobic chain, the polar character of the molecule as well as its molar volume.

- 5 The non-polar solvent or weakly polar solvent, which at 25°C is generally less than 5 wt % soluble in water, can be selected from the group consisting of alkylene glycol alkyl ethers having the formula:



wherein R'' is an alkylene group having 4 to 8 carbon atoms and x is 3 to 13 and y is 2 to 7 and can be selected from the group consisting of weakly water soluble polyoxyethylene alkyl ethers derivatives having the formula:



- 15 wherein x and is 6 to 18, more preferably 8 to 12 and y is equal to or lower than x/3 and esters having the formula:



- 20 wherein R and R<sub>1</sub> are alkyl groups having 7 to 24 carbon atoms, more preferably 8 to 20 carbon atoms. Some typical non-polar solvents or weakly polar solvents are decylacetate, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, disopropyl adipate, octyl lactate, dioctyl maleate, diethylene glycol mono octyl ether, Dobanol® 91 - 2.5 EO and mixtures thereof.

- 25 The concentration of the non-polar solvent or weakly polar solvent in the gelled near tricritical point composition is 1 to 15 wt %, more preferably 2 to 12 wt %.

The concentration of the low molecular weight amphiphile in the gelled near tricritical point composition is 1 to 23 wt %, more preferably 2 to 20 wt %.

- 30 The low molecular weight amphiphile of the instant gelled composition is a molecule composed of at least two parts which is capable of bonding with the polar solvent and the non-polar solvent. Increasing the molecular weight of the low

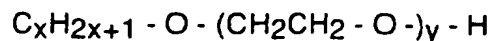
molecular weight amphiphile increases its water/oil coupling ability which means less low molecular weight amphiphile is needed to couple the polar solvent and the non-polar solvent or weakly polar solvent. At least one part is essentially hydrophobic, with a Hansen partial polar and hydrogen bonding solubility parameters less than 5 (MPa)<sup>1/2</sup>. At least one part is essentially water soluble, with Hansen partial hydrogen bonding solubility parameter equal or greater than 10 (MPa)<sup>1/2</sup>.

To identify the hydrophilic and hydrophobic parts, the low molecular weight amphiphilic molecule (amphiphile) must be cut according to the following rules: The hydrophobic parts should not contain any nitrogen or oxygen atoms; the hydrophilic parts generally contain the hetero-atoms including the carbon atoms directly attached to an oxygen or nitrogen atom.

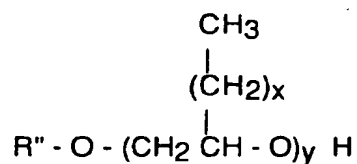
	Group	MW	$\delta_d$	$\delta_p$	$\delta_H$
15	-CH <sub>2</sub> -OH	31	15.5	16.1	25.4
	-CH <sub>2</sub> -NH <sub>2</sub>	30	13.8	9.3	16.7
	-CO-NH <sub>2</sub>	44	13	14.1	13.4
	-CH <sub>2</sub> -NH-CO-NH <sub>2</sub>	73	13.7	11.4	13.6
	-CH <sub>2</sub> -EO-OH	75	14.9	3.1	17.5
20	-CH <sub>2</sub> -EO <sub>2</sub> -OH	119	14.8	2.6	14.8
	-CH <sub>2</sub> -EO <sub>3</sub> -OH	163	14.7	2.1	13.3
	-CH <sub>2</sub> -EO <sub>4</sub> -OH	207	14.7	1.9	12.4
	-COO-CH <sub>3</sub>	59	13.7	8.3	8
	-CO-CH <sub>3</sub>	43	16.5	17.9	6.8
25	-C <sub>3</sub> H <sub>7</sub>	43	13.7	0	0
	-C <sub>4</sub> H <sub>9</sub>	57	14.1	0	0
	-C <sub>10</sub> H <sub>21</sub>	141	15.8	0	0

This table shows the solubility parameters for different groups. The first series can be used as the hydrophilic part of an amphiphile molecule, as the hydrogen bonding solubility parameter is always greater than 10. The last group can be used as the hydrophobic part of an amphiphile, as their polar and hydrogen bonding solubility parameters are below 1. The group in the middle (esters and ketones) cannot be used as a significant contribution to an amphiphile molecule. It is noteworthy that amphiphiles can contain ketone or ester functions, but these functions do not contribute directly to the amphiphile performance.  $\delta_d$  is the Hansen dispersion solubility parameter as measured at room temperature;  $\delta_p$  is the Hansen polar

solubility parameter as measured at room temperature;  $\delta_H$  is the Hansen hydrogen bonding solubility parameter as measured at room temperature. In particular preferred low molecular weight amphiphiles, which are present at a concentration of 5 to 60 wt %, more preferably 15 to 40 wt %, are selected from the group consisting of polyoxyethylene derivatives having the formula:



wherein x and/or y is 1 to 8, more preferably 1 to 6, polyols having 4 to 8 carbon atoms, polyamines having 5 to 7 carbon atoms, polyamides having 5 to 7 carbon atoms, alkanols having 2 to 4 carbon atoms and alkylene glycol alkyl ethers having the formula:



wherein R'' is an alkylene group having 4 to 8 carbon atoms and x is 0 to 2 and y is 1 to 5. The molecular weight of the low molecular weight amphiphile is 76 to 300, more preferably 100 to 250. Especially preferred low molecular weight amphiphiles are ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monohexyl ether and tetraethylene glycol monohexyl ether and mixtures thereof such as ethylene glycol monobutyl ether (EGMBE) and diethylene glycol monobutyl ether (DEGMBE) in a ratio of 1:2.

The near tricritical point gelled compositions formed from the previously described low molecular weight amphiphiles are surfactant free because these previously described low molecular weight amphiphiles are not classified as surfactants.

However, near tricritical point gelled compositions can be optionally formed from a polar solvent, a non-polar or weakly polar solvent and a surfactant on a mixture of a low molecular weight amphiphile and surfactant, when the surfactant is employed without a low molecular weight amphiphile, the surfactant is present in the gelled



composition at a concentration of 3.0 to 8.0 wt. percent. When the surfactant is employed in the gelled composition with the low molecular weight amphiphile the concentration of the surfactant is 0.1 to 6.0 weight percent and the concentration of the low molecular weight amphiphile is 1 to 25 wt. percent. The surfactants that are employed in the instant invention are selected from the group consisting of nonionics, anionics, amine oxides, cationics and amphoteric surfactants and mixtures thereof. An especially preferred nonionic surfactant is Dobanol 91-5. When the surfactant is used alone and without a low molecular weight amphiphile the surfactant must preferably have an HLB of 7 to 14. It is to be understood that surfactants are a subset of the set of amphiphiles. The low molecular weight amphiphiles do not form aggregates at an interface for example, the interface of oil and water, but rather the low molecular weight amphiphile is evenly distributed throughout the solution. Whereas a surfactant is prone to concentrate at the interfaces between different phases (air/liquid; liquid/liquid; liquid/solid) thereby forming aggregates at the interface and decreasing the interfacial tension between the above coexisting phases. For example a surfactant will form aggregates at an oil/liquid interface and the surfactant will not be evenly distributed throughout the solution.

The instant gelled near tricritical point compositions contain 0.2 to 3 wt. % , more preferably 0.25 to 2.6 wt. % of a low molecular weight noncrosslinked polymer selected from the group consisting of polyacrylic type polymer and a polyacrylamide type polymer, and mixtures thereof, wherein the polymer has a molecular weight of 20000 to 100000, more preferably 100000 to 500000.

The instant gelled compositions can also optionally include besides the polar solvent, the non-polar or weakly polar solvent and the water dispersible amphiphile, a water soluble acid at a concentration of 0.1 to 15.0 wt. percent, more preferably 1 to 10 wt. percent.

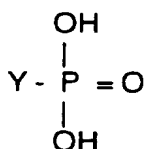
The active acidic component of the gelled near tricritical point composition can optionally be a carboxylic acid which is strong enough to lower the pH of the near tricritical point composition to the range of one to four. Various carboxylic acids can

perform this function, but those which have been found effective to remove soap scum and lime scale from bathroom surfaces, while still not destabilizing the composition, are polycarboxylic acids, and of these the dicarboxylic acids are preferred. Of the dicarboxylic acids group, which includes those of 2 to 10 carbon atoms, from oxalic acid through sebacic acid, suberic, azelaic and sebacic acids are of lower solubilities and therefore are not as useful in the present near tricritical point composition as the other dibasic aliphatic fatty acids, all of which are preferably saturated and straight chained. Oxalic and malonic acids, although useful as reducing agents too, may be too strong for delicate hard surface cleanings. Preferred such dibasic acids are those of the middle portion of the 2 to 10 carbon atom acid range, succinic glutaric, adipic and pimelic acids, especially the first three thereof, which fortunately are available commercially, in mixture. The diacids, after being incorporated in the invented near tricritical point composition may be partially neutralized to produce the desired pH in the near tricritical point composition for greatest functional effectiveness, with safety.

Citric acid can also be considered as an effective carboxylic acid.

Phosphoric acid is one of the additional acids that helps to protect acid-sensitive surfaces being cleaned with the present. Being a tribasic acid, it too may be partially neutralized to obtain a composition pH in the desired range. For example, it may be partially neutralized to the biphosphate, e.g.,  $\text{NaH}_2\text{PO}_4$ , or  $\text{NH}_4\text{H}_2\text{PO}_4$ .

Phosphonic acid, the other of the two additional acids for protecting acid-sensitive surfaces from the dissolving action of the dicarboxylic acids of the present compositions, apparently exists only theoretically, but its derivatives are stable and are useful in the practice of the present invention. Such are considered to be phosphonic acids, as that term is used in the specification. the phosphonic acids are of the structure:



wherein Y is any suitable substituent, but preferably Y is alkylamino or N-substituted alkylamino. For example, a preferred phosphonic acid component of the present compositions is aminotris-(methylenephosphonic) acid, which is of the formula  $N(CH_2PH_2O_3)$ . Among other useful phosphonic acids are ethylenediamine tetra-

5 (methylenephosphonic) acid, hexamethylenediamine tetra-(methylenephosphonic) acid, and diethylenetriamine penta-(methylenephosphonic) acid. Such class of compounds may be described as aminoalkylenephosphonic acids containing in the ranges of 1 to 3 amino nitrogens, 3 or 4 lower alkylenephosphonic acid groups in which the lower alkylene is of 1 or 2 carbon atoms, and 0 to 2 alkylene groups of 2 to 6  
10 carbon atoms each, which alkylene(s) is/are present and join amino nitrogens when a plurality of such amino nitrogens is present in the aminoalkylene phosphonic acid. It has been found that such aminoalkylenephosphonic acids which also may be partially neutralized at the desired pH of the near tricritical point composition, are of desired stabilizing and protecting effect in the invented cleaner, especially when present with  
15 phosphoric acid, preventing harmful attacks on European enamel surfaces by the diacid(s) components of the cleaner. Usually the phosphorus acid salts, if present, will be mono-salts of each of the phosphoric and/or phosphonic acid groups present.

Of all the organic acids which are of sufficient acidity effectively to attack soap scum and to convert it to a form which is readily removable from hard surfaces, such  
20 as ceramic tiles, Portland cement and acrylic latex grouts between the tiles, porcelain, porcelain enamel, glass, fiberglass and metal (such as chrome and nickel plated) surfaces, glutaric acid or a partially neutralized salt or ionized form thereof is highly preferred, because it performs effectively and has no significantly detrimental negative properties, but in some instances other acids capable of converting calcium and  
25 magnesium higher fatty acid soaps to acidic or partially neutralized form to assist in removing them from hard surfaces which they are staining (in the form of soap scum) may also be employed (when detrimental properties thereof, if any, are tolerable). Such acids will include those which do not form water insoluble calcium salts. For example, acetic acid, succinic acid, propionic acid and citric acid may be utilized in

some circumstances. However, citric acid is a sequestering acid and tends to remove calcium from calcium carbonate in the grout employed between adjacent ceramic tiles, which is detrimental to its use, and the other mentioned acids are often unsatisfactory because of unacceptable odors and/or because they result in human nasal and/or respiratory irritation. Of course, those acids which are toxic under the circumstance of use will also preferably be avoided. Therefore, glutaric acid is preferably utilized as such soap scum attacking acid. It may be (and usually is) subsequently partially neutralized to the desired pH range during manufacture of the invented cleaner but it is also within the invention to employ salts of such acid and to convert them to the desired pH, it being recognized that the products of both such operations are the same. Therefore, by reference to "partially neutralized glutaric acid" it is meant also to include such products resulting from partially acidifying glutaric acid salts (glutarates) or from directly incorporating the partially neutralized glutarates of desired pH with the other components of the cleaner.

The instant gelled composition can optionally contain 0.1 to 15 wt %, more preferably 1 to 5 wt % of a water soluble chaotropic additive which can be hydrotropic or kosmotropic. A hydrotropic agent weakens (salting-in effect) the structure of the water thereby making the water an improved solvent for the amphiphile, whereas a kosmotropic (lyotropic) agent strengthens (salting-out effect) the structure of the water thereby making water less of a solvent for the amphiphile. Typical hydrotropic agents are acetic acid, ethanol, isopropanol, sodium benzoate, sodium toluene sulfonate, sodium xylene sulfonate, ethylene glycol, propylene glycol, metal salts of iodide, metal salts of thiocyanates, metal salts of perchlorates, guanidinium salts. The use of the chaotropic additive can change the weight percentage of the polar solvent, amphiphile and non-polar solvent used to form the near tricritical point composition.

In addition to the recited components of the aqueous gelled near tricritical point compositions of the present invention, there may also be present adjuvant materials for dental, dishwashing, laundering and other detergency applications, which materials may include: foam enhancing agents such as lauric or myristic acid

diethanolamide; foam suppressing agents (when desired) such as silicones, higher fatty acids and higher fatty acid soaps; preservatives and antioxidants such as formalin and 2,6-ditert-butyl-p-cresol; pH adjusting agents such as sulfuric acid and sodium hydroxide; perfumes; and colorants (dyes and pigments).

5           The instant gelled compositions can optionally contain an inorganic or organic builder salt provided that the salt is not present at a concentration that destroys the character of the tricritical point compositions. The builder salt is generally present at a concentration of 1 to 30 wt. %, more preferably 2 to 10 wt. %. The builder salt is selected from the group consisting of isoserine diacetate acid, alkali metal carbonates, 10 alkali metal bicarbonates, alkali metal citrates, alkali metal salts of a polyacrylic acid having a molecular weight of 500 to 4,000, alkali metal tartarates, alkali metal gluconates, alkali metal silicates, alkali metal tripolyphosphates and alkali metal pyrophosphates and mixtures thereof. The maximum concentration of the builder salt in the gelled tricritical point composition is determined by and limited by the solubility 15 of the builder salt in the water phase, wherein the builder salt is completely dissolved in the water phase.

The aqueous gelled near tricritical point compositions can be used in forming cleaning compositions containing enzymes and/or bleachants such as fabric detergent compositions or automatic dishwashing compositions which can contain 20 bleachants, at least one enzyme, and a suitable phosphate or non-phosphate builder system.

The variations in formulas of the gelled compositions within the invention which are in the tricritical or near tricritical state are easily ascertainable, and the invention is readily understood when reference is made to this specification, including the working 25 examples thereof, taken in conjunction with the phase diagrams.

In the previous description of the components of the invented compositions and proportions thereof which may be operative, boundaries were drawn for preferred compositions within the invention, but it will be evident that one seeking to manufacture the invented near tricritical point compositions will select proportions of

components indicated by the phase diagrams for the particular compositions, so that the desired compositions will be within the near tricritical area. Similarly, the gelled tricritical point compositions selected should be such that upon contact with water, the lipophilic soil will be removed from a substrate.

5 For plotting of the phase diagrams and in experiments undertaken by the inventors to establish the formulas of the desired gelled tricritical point compositions, many different compositions within the invention were made and were characterized.

To make the gelled near tricritical point compositions of the invention is relatively simple because they tend to form spontaneously with little need for the  
10 addition of energy to promote transformation of the tricritical state. However, to promote uniformity of the composition, mixing will normally be undertaken and it has been found desirable, but not compulsory, to first mix the amphiphile and water together, followed by admixing of the non-polar solvent or weakly solvent component. It is not usually necessary to employ heat and most mixings are preferably carried out  
15 at 20-25°C or higher.

Pre-spotting and manual cleaning uses of the invented gelled near tricritical point compositions are uncomplicated, requiring no specific or atypical operations. Thus, such gelled near tricritical point compositions may be employed in the same manner as other liquid pre-spotting and detergent compositions.

20 The invented gelled near tricritical point compositions may be applied to such surfaces with a cloth or sponge, or by various other contacting means, but it is preferred to apply them, depending on their viscosity. Such application may be applied onto hard surfaces such as dishes, walls or floors from which lipophilic (usually greasy or oily) soil is to be removed, or may be applied onto fabrics such as  
25 laundry which has previously been stained with lipophilic soils such as motor oil. The invented gelled compositions may be used as detergents and as such may be employed in the same manner in which liquid detergents are normally utilized in dishwashing, floor and wall cleaning, and laundering, but it is preferred that they are employed as pre-spotting agents too, in which applications they are found to be

extremely useful in loosening the adhesions of lipophilic soils to substrates, thereby promoting much easier cleaning with application of more of the same invented detergent compositions or by applications of different commercial detergent compositions in liquid, bar or particulate forms.

5

### Examples

The following examples illustrate but do not limit the invention. Unless otherwise indicated, all parts in these examples, in the specification and in the appended claims are by weight percent and all temperatures are in °C.

The formulas A through E were prepared according to the following procedure:

10

Compositions A through E were made by firstly incorporate the thickener system in water to ensure the best dispersion and ideally allow it to thicken. The amphiphile is then added, followed by the oil and finally the perfume.

### EXAMPLE 1

COMPOSITION	A	B	C	D	E
Water	82	80	81.6	80.71	81.4
d-limonene	4	4	4	4	4
Triethylene glycol hexyl ether	13	13	13	13	13
Acusol 820		2	0.4		
Sepigel 501	11.5			1.29	0.6
Perfume	1.0	1.0	1.0	1.0	1.0
Brookfield viscosity 25°C, spindle #4, 20 rpms	10	1800	150	4950	550
Tough degreasing	Std	slightly worse	equal	equal	equal
Dried on food	Std.	equal	equal	equal	equal
Tar lifting (seconds)		Std	equal	equal	equal
Tar lifting on inclined surface (45°C) std.	Std.	better	better	better	better

15

#### A. Degreasing Test

##### Test Purpose

The degreasing test compares the grease removal ability of two products.

It aims to reproduce how a housewife cleans greasy dirt's from usual surfaces

20

in the home e.g. counter tops in the kitchen. Considering the habits of housewives - to allow in some cases some contact time to let the product act (prespotting) - products were also evaluated for tough grease removal after a short contact time (2 min.).

Test Description

A washability machine (Gardner) is made from a carrier equipped with two twin current vegetable sponges moving in phase and with the same pressure on the soiled area. Surface: Formica tiles.

5 Soil composition

Tough degreasing: Hydrogenated beef tallow 10% solution in chloroform (Radia 3059 grade from Oleofina - Belgium).

Standard degreasing: Beef tallow ("Blanc de boeuf - Ossewit" grade from N.V. Vandemoortele - Belgium) + 5% hydrogenated tallow (Radia 3059) in chloroform.

10 Both grease solutions are dyed with 0.05% of Fat Blue B from Cassella.

Soiling method

The surfaces are cleaned thoroughly, rinsed with acetone and water and then dried. The solutions are sprayed on the Formica tiles and then allowed to dry for 15' before evaluation.

15 Evaluation

Add 2.5 g on each sponge initially wet with tap water. For each product, the number of strokes is recorded, the product removing 95% of the soil with less strokes being better. Three replicates are run.

B. Dried-on food20 Test purpose

The test compares the baked-on food removal ability of two products.

Test description: Gardener machine as for degreasing. Surface: white enamel tiles.

Soil composition

25 Its composition is as follows: 31.5g Fama margarine; 15g egg yolk; 2g beef extract; 1.5g Maiezena flour; 62.5g water.

Soiling method

The mixed food soil is applied with a paint brush on the white enamel tile and allow to bake 10 minutes at 270°C.



Evaluation

For each product, the number of strokes is recorded, the product removing the soil with less strokes being better.

C. Tar5 Test purpose

Tar is not a current soil especially at home. However, tar is a very tough soil to remove especially when aged. Then all usual cleaners fail and only SWC technology works. It was used to evidence "critical" phenomenon and cleaning mechanism.

Test description

10 The cleaning of tar is evaluated visually. It is the time required to perceive the first clear signals of tar lifting action i.e. apparition of cracks in the soil revealing the white ceramic surface and signs of soil disaggregation.

Soil composition and soiling method

15 Tar (Mulex liquid ex-Asphalco) is dissolved at saturation in tri-chloroethylene. The dark brown solution is paint homogeneously on a ceramic tile. The soiled tile is allowed to dry (evaporation of the solvent) for at least 3 days to harden enough.

Evaluation

20 One drop of neat product is applied on the soiled surface. Time to record lifting effect is recorded (at least three replicates per product), the shorter the time the stronger the product.

The invention has been described with respect to various embodiments and illustrations of it but is not to be considered as limited to these because it is evident that one of skill in the art with the present specification before him/her will be able to utilize substitutes and equivalents without departing from the invention.

WHAT IS CLAIMED IS

1. A liquid gelled cleaning composition having a surface tension of 10 to 35 mN/m and incorporating 0.2 to 4.0 wt. % of a low molecular weight noncrosslinked polymer selected from the group of polyacrylic acid type polymers and polyacrylamide type polymers and mixtures thereof, and at least a polar solvent, a water soluble or water dispersible low molecular weight amphiphile and a non-polar or weakly polar solvent and deriving from three co-existing liquid phases which are capable of being converted into one single phase according to a reversible equilibrium, or to make the three co-existing liquid phases merge together into one continuum to form said composition, wherein the first phase is the most abounding with the polar solvent, the second phase is the most abounding with the water soluble or water dispersible low molecular weight amphiphile and the third phase is the most abounding with the non-polar solvent or weakly polar solvent, and the interfacial tension between said first phase and said second phase is 0 to  $1 \times 10^{-3}$  mN/m, and the interfacial tension between second phase and third phase is a 0 to  $1 \times 10^{-3}$  mN/m, and the interfacial tension between first phase and third phase is 0 to  $1 \times 10^{-3}$  mN/m, wherein said polar solvent is at a concentration 55 to 95 wt. %.

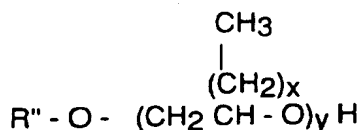
2. A gelled composition according to Claim 1, wherein the polar solvent is water at a concentration of 55 to 95 wt %, the amphiphile being an organic compound having a water insoluble hydrophobic portion which has a partial polar parameter and hydrogen bonding parameter, both of which are less than  $5 \text{ (MPa)}^{1/2}$ , and a water soluble hydrophilic portion which has a partial hydrogen bonding solubility parameter greater than  $10 \text{ (MPa)}^{1/2}$ ; said amphiphile being present at a concentration of 1 to 23 wt %; and said non-polar solvent or weakly polar solvent having a dispersion solubility parameter greater than  $10 \text{ (MPa)}^{1/2}$  and a hydrogen bonding solubility parameter of less than  $15 \text{ (MPa)}^{1/2}$ , said non-polar solvent or weakly polar solvent being present at a concentration of 2 to 15 wt %.

3. A gelled composition according to Claim 2, wherein said low molecular weight amphiphile is selected from the group consisting of alkylene glycol alkyl ethers, polyoxyethylene derivatives having the formula:

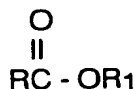


5 wherein x is 4 to 8 and y is 1 to 6. polyols having 4 to 8 carbon atoms, polyamines having 5 to 7 carbon atoms, polyamides having 5 to 7 carbon atoms, and alkanols having 2 to 4 carbon atoms.

4. A gelled composition according to Claim 3, wherein said non-polar solvent or weakly polar solvent is selected from the group consisting of alkylene glycol  
10 alkyl ethers having the formula:



15 wherein R'' is an alkylene group having 4 to 8 carbon atoms and x is 3 to 13 and y is 2 to 7 and esters having the formula:



20 wherein R and R<sub>1</sub> are alkyl groups having 7 to 24 carbon atoms.

5. A gelled composition according to Claim 1, wherein said polar solvent is water.

6. A gelled composition according to Claim 1, wherein said composition is sprayable by a hand operated pump sprayer.

25 7. A gelled composition according to Claim 1, containing at least one solid particle and/or immiscible liquid in said composition.

8. A gelled composition according to Claim 5, wherein said low molecular weight amphiphile is triethylene glycol monohexyl ether.

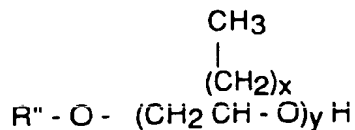
9. A gelled liquid cleaning composition having a surface tension of 10 to 35  
30 mN/m and incorporating 0.2 to 4.0 wt. % of a low molecular weight noncrosslinked polymer selected from the group consisting of polyacrylic acid type polymers and

polyacrylamide type polymers and mixtures thereof, and at least a polar solvent, a water soluble or water dispersible surfactant and a non-polar or weakly polar solvent and deriving from three co-existing liquid phases which are capable of being converted into one single phase according to a reversible equilibrium, or to make the three coexisting liquid phases merge together into one continuum to form said composition, wherein the first phase is the most abounding with the polar solvent, the second phase is the most abounding with the water soluble or water dispersible surfactant and the third phase is the most abounding with the non-polar solvent or weakly polar solvent, and the interfacial tension between said first phase and said second phase is 0 to  $1 \times 10^{-3}$  mN/m, and the interfacial tension between second phase and third phase is a 0 to  $1 \times 10^{-3}$  mN/m and the interfacial tension between the first phase and the third phase is 0 to  $1 \times 10^{-3}$  mN/m, wherein the concentration of the polar solvent is 55 to 95 wt. %.

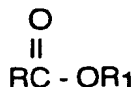
10. A gelled composition according to Claim 9, wherein the polar solvent is water, the amphiphile being an organic compound having a water insoluble hydrophobic portion which has a partial polar parameter and hydrogen bonding parameter, both of which are less than 5 (MPa)<sup>1/2</sup>, and a water soluble hydrophilic portion which has a partial hydrogen bonding solubility parameter greater than 10 (MPa)<sup>1/2</sup>; said amphiphile being present at a concentration of 1 to 23 wt. %; and said non-polar solvent or weakly polar solvent having a dispersion solubility parameter greater than 10 (MPa)<sup>1/2</sup> and a hydrogen bonding solubility parameter of less than 15 (MPa)<sup>1/2</sup>, said non-polar solvent or weakly polar solvent being present at a concentration of 2 to 15 wt. %.

11. A gelled composition according to Claim 10, wherein said non-polar solvent or weakly polar solvent is selected from the group consisting of alkylene glycol alkyl esters having the formula:

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- 5 wherein R'' is an alkylene group having 4 to 8 carbon atoms and x is 3 to 13 and y is 2 to 7 and esters having the formula:



- 10 wherein R<sub>1</sub> and R are alkyl groups having 7 to 24 carbon atoms.

12. A gelled composition according to Claim 11, wherein said polar solvent is water and is present in the composition at a concentration of 15 to 85 wt. %.

13. A gelled composition according to Claim 10, wherein said composition is sprayable by a hand operated pump sprayer.

- 15 14. A gelled composition according to Claim 10 containing at least one solid particle and/or immiscible liquid in said composition.

15. A gelled composition according to Claim 10, wherein said non-polar solvent or weakly polar solvent is an aliphatic hydrocarbon having 6 to 16 carbon atoms.

- 20 16. A gelled composition according to Claim 10, wherein said surfactant is an anionic surfactant.

17. A gelled liquid cleaning composition having a surface tension of 10 to 35 mN/m and incorporating at 0.2 to 4.0 wt. % of a low molecular weight noncrosslinked polymer selected from the group consisting of polyacrylic acid type polymers and polyacrylamide type polymers and mixtures thereof, and least a polar solvent, a water soluble or water dispersible low molecular weight amphiphile a non-polar or weakly polar solvent and a water soluble acid and deriving from three co-existing liquid phases which are capable of being converted into one single phase according to a reversible equilibrium, or to make the three coexisting liquid phases merge together

- 25 30 into one continuum to form said composition, wherein the first phase is the most abounding with the polar solvent, the second phase is the most abounding with the

water soluble or water dispersible low molecular weight amphiphile and the third phase is the most abounding with the non-polar solvent or weakly polar solvent and the water soluble acid is contained within the first phase the second phase and the third phase and the interfacial tension between said first phase and said second phase is 0 to  $1 \times 10^{-3}$  mN/m, and the interfacial tension between second phase and third phase is a 0 to  $1 \times 10^{-3}$  mN/m, and the interfacial tension between first phase and third phase is 0 to  $1 \times 10^{-3}$  mN/m, wherein the concentration of the polar solvent is 55 to 95 wt. %.

18. A gelled composition according to Claim 17, wherein the polar solvent is water, the amphiphile being an organic compound having a water insoluble hydrophobic portion which has a partial polar parameter and hydrogen bonding parameter, both of which are less than  $5 \text{ (MPa)}^{1/2}$ , and a water soluble hydrophilic portion which has a partial hydrogen bonding solubility parameter greater than 10  $(\text{MPa})^{1/2}$ ; said amphiphile being present at a concentration of 1 to 23 wt. %; and said non-polar solvent or weakly polar solvent having a dispersion solubility parameter greater than 10  $(\text{MPa})^{1/2}$  and a hydrogen bonding solubility parameter of less than 15  $(\text{MPa})^{1/2}$ , said non-polar solvent or weakly polar solvent being present at a concentration of 2 to 15 wt. %.

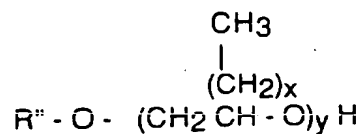
19. A gelled composition according to Claim 18, wherein said low molecular weight amphiphile is selected from the group consisting of alkylene glycol alkyl ethers, polyoxyethylene derivatives having the formula:



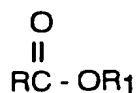
wherein x is 4 to 8 and y is 1 to 6. polyols having 4 to 8 carbon atoms, polyamines having 5 to 7 carbon atoms, polyamides having 5 to 7 carbon atoms, and alkanols having 2 to 4 carbon atoms.

20. A gelled composition according to Claim 19, wherein said non-polar solvent or weakly polar solvent is selected from the group consisting of alkylene glycol alkyl esters having the formula:

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- 5 wherein R'' is an alkylene group having 4 to 8 carbon atoms and x is 3 to 13 and y is 2 to 7 and esters having the formula:



- 10 wherein R<sub>1</sub> and R are alkyl groups having 7 to 24 carbon atoms.

21. A gelled composition according to Claim 17, wherein said polar solvent is water.

22. A gelled composition according to Claim 17, containing at least one solid particle and/or immiscible liquid in said composition.

- 15 23. A gelled composition according to Claim 21, wherein said low molecular weight amphiphile is triethylene glycol monohexyl ether.

# INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/US 96/16862

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D17/00 C11D3/37 C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 27035 A (UNILEVER PLC ; UNILEVER NV (NL)) 12 October 1995	1,9,10, 12-15,17
Y	see page 6, line 34 - page 7, line 3; claims	1-23
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

10 February 1997

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18.02.97

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Information on patent family members

International Application No

PCT/US 96/16862

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